

Notes

Viscosity studies of some 1:1 electrolytes in acetic acid at 25°C

V P Kapila, C M Gupta & S P Jauhar*

Department of Chemistry, Panjab University,
Chandigarh 160 014

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The viscosities of lithium, sodium, potassium, cesium and ammonium acetates, tetramethyl-, tetraethyl-, tetrapropyl-, tetrabutyl-, tetrapentyl- and tetrahexyl-ammonium bromides and sodium and tetrabutylammonium iodides have been measured in the concentration range $0.5-8.4 \times 10^{-2} \text{ mol l}^{-1}$ in acetic acid at 25°C. The data have been analysed by the Jones-Dole equation, and viscosity B-coefficients are found to be positive in acetic acid. Ionic B-coefficients are obtained by splitting the B-coefficients of tetrabutylammonium bromide and tetrapentylammonium bromide into the contributions due to individual ions in terms of their ionic radii. The solvation behaviour of ions in acetic acid has been interpreted in terms of their ionic sizes.

Viscosity measurements, like other transport properties of electrolyte solutions, provide useful information about ion-solvent interactions and are gaining considerable importance in the case of nonaqueous solvents¹⁻⁴. Though acetic acid is one of the most extensively investigated nonaqueous solvents⁵, viscosity studies of electrolytes in this solvent are scanty. Lakshminarayana *et al.*⁶ have measured the relative viscosities and densities of solutions of only three salts, lithium, sodium and potassium acetates in acetic acid to calculate the viscosity B-coefficients and partial molal volumes of the ions.

Acetic acid at room temperature is a clear, colourless and highly associated liquid. It has a convenient liquid range of about 100°, relatively low viscosity (1.16 cP), low dielectric constant (6.21) and small dipole moment. In the present study, viscosity measurements of some uni-univalent electrolytes such as alkali metal acetates and tetraalkylammonium bromides, which have appreciable solubility in acetic acid have been carried out at 25°C to understand the nature of these electrolytes in this medium and to throw light on ion solvent interactions.

Experimental

Acetic acid (BDH, AR grade) was purified by fractional freezing followed by refluxing with acetic anhydride for several hours and was finally fraction-

ally distilled. The middle fraction distilling at 115-116°C was collected (sp. conductance = $5-6 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$, density = $1.04365 \text{ g cm}^{-3}$ and viscosity = 1.16 cP, all at 25°C). Freshly distilled solvent was used for each experimental run and its physical constants were checked.

Lithium, sodium, potassium and cesium acetates were of AR or equivalent grade and were dried at 140°C for 3-4 h. These were cooled *in vacuo* over phosphorus pentoxide. Tetraalkylammonium halides and ammonium acetate of AR grade were used as such after drying *in vacuo*. Sodium iodide (LR grade) was recrystallised from water-ethanol mixture and dried for 5-6 h *in vacuo* at 70°C. All the salts were finely ground and dried *in vacuo* prior to their use.

Viscosities were measured with a modified Ubbelohde's capillary type viscometer as described earlier⁷ (experimental accuracy = $\pm 0.002 \text{ cP}$). The densities were measured⁷ using a bicapillary pycnometer (accuracy = $\pm 0.0001 \text{ g cm}^{-3}$). All the measurements were carried out in an electrically controlled water thermostat maintained at $25.00 \pm 0.01^\circ\text{C}$.

Results and discussion

Densities and viscosities of solutions of CH_3COOLi , CH_3COONa , CH_3COOK , $\text{CH}_3\text{COONH}_4$, CH_3COOCs , NaI , Me_4NBr , Et_4NBr , Pr_4NBr , Bu_4NBr , Bu_4NI , Pen_4NBr and Hex_4NBr have been measured in the concentration range $0.5-8.4 \times 10^{-2} \text{ mol l}^{-1}$ in acetic acid at 25°C. The viscosity data have been analysed using the Jones-Dole equation⁸ in the form

$$\eta/\eta_0 = 1 + AC^{1/2} + BC \quad \dots (1)$$

where η and η_0 are the viscosities of the electrolyte solution and of the pure solvent respectively, C is the molar concentration and A and B are viscosity coefficients characteristic of ion-ion and ion-solvent interactions respectively.

The equation (1) may be rearranged as $(\eta/\eta_0 - 1)/C^{1/2} = A + BC^{1/2} \quad \dots (2)$ so that viscosity A and B coefficients can be calculated from the $(\eta/\eta_0 - 1)/C^{1/2}$ versus $C^{1/2}$ plots as the intercept and the slope respectively. The plots were found to be linear over the whole concentration range and the values of A and B were calculated by the least squares method (Table 1).

The viscosity A coefficient can also be calculated theoretically⁹ from the knowledge of conductance data and the physical properties of the solvent.

Table 1—Viscosity A and B coefficients of Jones-Dole equation for some 1:1 electrolytes in acetic acid at 25°C

Electrolyte	$A(l^{1/2} \text{ mol}^{-1/2})$	$B(l \text{ mol}^{-1})$
CH_3COOLi	0.04	0.80
CH_3COONa	0.02	1.00
CH_3COOK	0.01	0.87
$\text{CH}_3\text{COONH}_4$	0.01	0.72
CH_3COOCs	0.00	0.60
Me_4NBr	0.01	0.58
Et_4NBr	0.01	0.61
Pr_4NBr	0.01	0.65
Bu_4NBr	0.02	0.68
Pen_4NBr	0.02	0.83
Hex_4NBr	0.01	0.87
Bu_4NI	0.01	0.99
NaI	0.02	1.20

However, because of the lack of ionic conductance data of electrolytes in acetic acid, the theoretical A coefficients could not be calculated for the sake of comparison.

The viscosity B coefficients for all the electrolytes in acetic acid are positive. Lakshminarayana and Krishnan⁶ have also reported viscosity B coefficient values for CH_3COOLi , CH_3COONa and CH_3COOK in acetic acid at 35°C. Our viscosity B-values at 25°C are slightly higher than those reported by these workers, but the trend is the same.

Ionic viscosity B coefficients

To have a better understanding of the ion-solvent interactions, it is necessary to split the viscosity B coefficients into the individual ionic B coefficients B_+ and B_- . However, there is no experimental method available to split viscosity B-coefficients and, therefore, the division has to be arbitrary. A number of methods have been suggested for doing this¹⁰. Most of these methods depend upon the choice of a reference electrolyte for which cation-solvent and anion-solvent interactions may be considered equal. In our previous publications^{4,11} we have used triisooamylbutylammonium tetraphenylboride and tetrabutylammonium tetraphenylboride as the reference salts. However, because of their poor solubilities in acetic acid, the salts could not be used as reference electrolytes.

In the present studies, ionic B-coefficients were calculated by using the equations:

$$B(\text{Bu}_4\text{N}^+) - B(\text{Pen}_4\text{N}^+) = B(\text{Bu}_4\text{NBr}) - B(\text{Pen}_4\text{NBr}) \quad \dots (3)$$

Table 2—Ionic $B_{\pm}$ coefficients ($l \text{ mol}^{-1}$) in acetic acid at 25°C

Ion	Ionic B values ($B_{\pm}$)
Li^+	0.39
Na^+	0.59
K^+	0.46
NH_4^+	0.31
Cs^+	0.19
Me_4N^+	0.28
Et_4N^+	0.31
Pr_4N^+	0.35
Bu_4N^+	0.38
Pen_4N^+	0.53
Hex_4N^+	0.57
Br^-	0.30
I^-	0.61
Ac^-	0.41

$$\text{and } \frac{B(\text{Bu}_4\text{N}^+)}{B(\text{Pen}_4\text{N}^+)} = \frac{r^3(\text{Bu}_4\text{N}^+)}{r^3(\text{Pen}_4\text{N}^+)} = \left(\frac{0.385}{0.430} \right)^3 \quad \dots (4)$$

based on the lack of solvation of large tetraalkylammonium ions R_4N ($\text{R} > \text{Bu}$). This method has been used by some other workers also¹².

Solving the above equation for $B(\text{Bu}_4\text{NBr})$ and $B(\text{Pen}_4\text{NBr})$, we got $B(\text{Bu}_4\text{N}^+) = 0.38$, $B(\text{Pen}_4\text{N}^+) = 0.53$ and $B(\text{Br}^-) = 0.30$. The value of $B(\text{Bu}_4\text{N}^+)$ was used to calculate the ionic B-value for I^- ion from the B value for Bu_4NI . The $B(\text{I}^-)$ was further used to calculate $B(\text{Na}^+)$ from B value of NaI . These values were further used to calculate ionic viscosity B coefficients of all the other ions. The results are recorded in Table 2.

An inspection of Table 2 reveals that the viscosity B-coefficients for the cations follow the order:

$$\text{Na}^+ > \text{K}^+ > \text{Li}^+ > \text{Cs}^+$$

$$\text{Me}_4\text{N}^+ < \text{Et}_4\text{N}^+ < \text{Pr}_4\text{N}^+ < \text{Bu}_4\text{N}^+ < \text{Pen}_4\text{N}^+ < \text{Hex}_4\text{N}^+$$

Except for Li^+ ion, the order of decreasing viscosity B-coefficients is opposite to the order of decreasing ionic radii suggesting that smaller alkali metal ions are more solvated in acetic acid and solvation of ion decreases with increase in ionic radii. The anomalous behaviour of Li^+ ion has been observed by Lakshminarayana *et al.*⁶ also at 35°C. On the other hand, the B-coefficients of large tetraalkylammonium ions decrease with the increase in ionic radii. This is due to lack of solvation of large tetraalkylammonium ions and increase in crystallographic radii. Similar behaviour of tetraalkylammonium ions has also been noticed by other workers^{7,13,14}.

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